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W. Michael Yim

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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of
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ABSTRACT

The purpose of this investigation is to determine whether ferromagnetic alloys exist in the ternary system Cu-Mn-Zn analogous to the other Heusler alloys.

The work in this thesis is a preliminary investigation on these alloys using a common metallographic research technique and augmented with X-ray methods.

Alloys of various compositions were prepared, and their magnetic properties were studied. The results of this investigation showed the epsilon and beta phases were ferromagnetic as were reported previously. Their degrees of ferromagnetism were however, very small in comparison with common ferromagnetic materials such as iron and nickel.

Many new problems arose from the X-ray work pertaining to the structure of the ferromagnetic Cu-Mn-Zn alloys, which await further investigation for the complete solution.

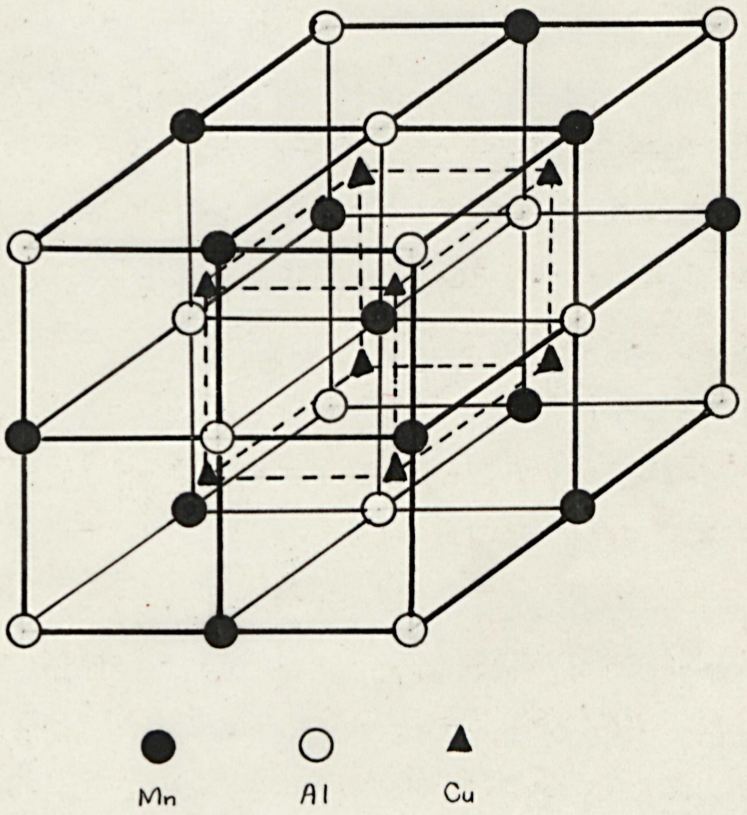
I. INTRODUCTION:

In 1898, F. Heusler found that ternary alloys of copper, manganese, and tin became ferromagnetic on proper treatment, although each individual constituent is not ferromagnetic. His discovery stimulated numerous investigators and since then a great deal of research has been carried out.(1)

It was early found that tin could be replaced by aluminum, arsenic, antimony, bismuth, and boron; also copper could be replaced by silver.(2) All these alloys have been known as "Heusler alloys." However, no proper explanation was given as to the source of ferromagnetism of these alloys until the early 30's when an extensive X-ray analysis was employed in the investigation of these alloys.

In 1933, O. Heusler found that the ferromagnetism of the Heusler alloys of Cu-Mn-Al was associated with the ternary beta phase, body-centered cubic structure, and most of the freshly quenched ferromagnetic beta alloys showed superlattice lines. From the X-ray results, he concluded that ferromagnetic beta alloys were ordered, and in the ideally ordered beta alloy whose composition corresponds with Cu_2MnAl, the copper atoms occupy the center position of a cube; whereas, the

FIG-1



ATOMIC ARRANGEMENT IN ORDERED Cu_2MnAl

after DR. F.A. HAMES

manganese and the aluminum atoms alternately occupy the cube corners as shown in Fig. 1. Furthermore, each change from perfection, either by a redistribution of atoms in Cu_2MnAl or by introduction of new atoms with a change in composition, the magnetization and Curie point were lowered.(3)

His findings were later confirmed by a number of scientists; among whom are Dr. Carapella who worked on the Cu-Mn-Sn system,(4) and Dr. Hames on the Cu-Mn-In system.(5) Prof. Valentiner also reported the replacement of aluminum and tin by indium in the Heusler alloys.(6) According to Hume-Rothery and co-workers, the electron concentration of the phase next to the alpha, i.e., the beta is approximately 1.5 in many alloys of copper, silver, and gold with elements of the B subgroups.(7) However, many exceptions were reported in the beta phase of the Heusler alloys.(4,8) Many investigators, few of them were mentioned above, confirmed O. Heusler's conclusion that the ordered beta phase is essentially responsible for the ferromagnetism of the Heusler alloys. Klyucharev, however, reported that the ferromagnetism of the Heusler alloys was not due to the ordered beta phase. He found that an alloy containing 16% Al in the system of Al-Cu-Mn was ferromagnetic in the face-centered-cubic structure rather than in the

body-centered-cubic structure.(8)

The chemical similarities of zinc with tin, aluminum, and indium, and also the existence of beta phase in the binary system of Cu-Zn, suggest the possible existence of ferromagnetic alloys in the ternary system Cu-Mn-Zn. The purpose of this investigation is to determine whether ferromagnetic alloys exist in the Cu-Mn-Zn system, and to correlate the ferromagnetism with the phase in the system.

A complete investigation requires a considerable length of time; hence, with a limited time, it was possible to obtain only general information of the ferromagnetic alloys in the Cu-Mn-Zn system in this investigation.

II. PREVIOUS WORK:

In 1926, O. Heusler reported that the ternary beta and epsilon solid solutions of the Cu-Mn-Zn system are ferromagnetic, although, to a much smaller degree than other Heusler alloys. The ferromagnetism was most pronounced for the alloy containing 22% Mn, 22% Cu, and 56% Zn. "Quenching from above 500C (932F) produced reguli with polar magnetism; however, after the distintegration of the beta crystals, the alloy becomes less ferromagnetic than before."(9) The atomic composition of this alloy was approximately $Cu_2Mn_2Zn_5$.

However, the early work on this alloy system is fragmentary, and unfortunately, based on alloys with impure grades of manganese which introduced significant amounts of iron, silicon, aluminum, and carbon. No theoretical explanation was given on the origin of the ferromagnetism.

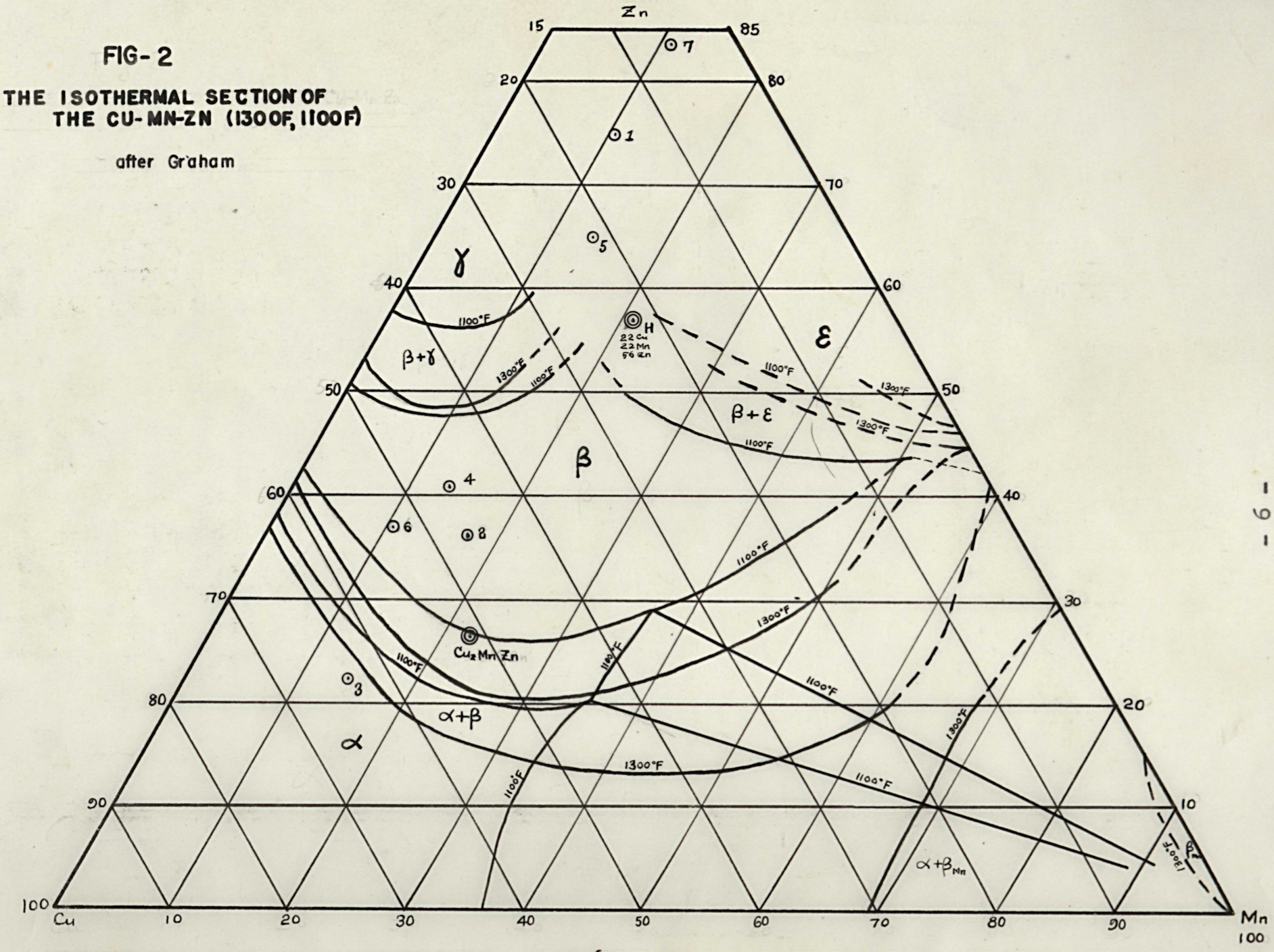
More recently, metallographic research was carried out in the determination of the ternary phase diagram and the mechanical properties of the Cu-Mn-Zn alloys rather than ferromagnetic properties.

In 1939, K. Moeller reported that the hexagonal-close-packed phase, formed at approximately 30 atomic per cent Mn in the Mn-Zn system, forms ternary solid

FIG- 2

THE ISOTHERMAL SECTION OF THE CU-MN-ZN (1300F, 1100F)

after Graham



solutions with the hexagonal epsilon phases in the Ag-Zn and Cu-Zn systems.[10]

From 1944 to 1949, the United States Bureau of Mines has conducted investigation on the ternary system Cu-Mn-Zn. Then primary object was confined to the investigation of the mechanical properties and in determination of the ternary equilibrim diagrams.[11,12,13,14,15] In 1949, T. R. Graham and co-workers published ternary phase diagrams of isothermal sections ranging from 1100F to 1500F as shown in Fig. 2.[16] In these diagrams, the phases of alloys containing over 60% zinc were not shown.

According to their diagram, the ternary beta phase exists over a long range, and the alloy of Cu_2MnZn falls in beta region at temperatures from 1200F to 1500F. The most ferromagnetic alloy previously reported by O. Heusler is composed of the beta and epsilon phases at 1100F in their diagrams.

No quantitative data was reported concerning the value of magnetic saturation and the X-ray results on the alloys of Cu-Mn-Zn.

III. EXPERIMENTAL WORK:

The alloys were prepared from electrolytic copper of 99.98% purity, electrolytic manganese of 99.90% purity, produced by the Electro-Manganese Corporation, Knoxville, Tenn., and electrolytic zinc of 99.97% purity. Typical analysis of manganese and zinc by their manufactures are given in Table 1. The purity of manganese is noteworthy, since this metal introduced most of impurities to the alloys previously used.

Table 1

Chemical Analysis of Metals Used

Mn	Zn
Fe-----Max.0.02%	Pb,Fe,insol.--0.03%
S -------- 0.03%	
C --------- Nil	
Si,Al,Ni ---0.05%	
Co,Cu	

(A) Preparation of Alloys:

Master alloys of the composition of Cu_2Mn (69.8 wt.% Cu, 30.2 wt.% Mn) and that of 50 wt.% Cu, 50 wt.% Mn were prepared. The alloys were then prepared by melting together master alloys and zinc proportioned

according to the amounts calculated, in a high-frequency induction furnace.

A silica crucible was first used; however, molten manganese attacked the crucible severely and it was found impossible to melt the alloys in silica crucible. Prof. Smith suggested graphite crucible, and it was used with success. Dr. Carapella and Dr. Hames reported that high purity alumina crucible was also used satisfactorily.(4,5)

Because of a considerable difference in melting point between zinc, copper, and manganese, shown in Table II, it was impossible to obtain the alloys of the intended composition.

Table II

Melting Point and Boiling Point of Metals Used (°C)

	Cu	Mn	Zn	Cu_2Mn	Cu, 50 wt% Mn, 50 wt%
m.p.	1083	1240	419.4	880	970
b.p.	2325	2150	907.7	---	---

However, the author later found that T. R. Graham and J. R. Long recommended a melting procedure of the Cu-Mn-Zn alloys as follows.(11)

"The recommended melting procedure consists of first preparing a Mn-Zn hardener of a desired ratio and adding the hardener to molten copper. Use of the

hardener is a material aid in obtaining specific alloy compositions, and it is easily prepared by melting zinc under a sodium borate cover and gradually washing the manganese cathode chips into solution, using a Cu-Mn stirring rod to push the manganese under the surface of the bath. Electrolytic manganese will dissolve in zinc with no serious difficulty up to 35%, and the only precaution necessary is to keep the temperature below the flare point of the zinc. Ordinary manganese was more difficult to dissolve, and a considerably longer time was required. These alloys have been made satisfactorily also by direct alloying and by using a Cu-Mn hardener. However, the Mn-Zn hardener has the advantage of simplicity in preparation and good control of chemical composition, and requires only the single addition to molten copper to produce the alloys."

The chemical analysis of the alloys, as made by Mr. C. J. Bartzen, analyst of the Bureau of Mines, are given in Table III. The data are plotted in Fig. 2.

Table III

Composition of Alloys

Alloy No.	Cu	Zn	Mn (by Diff.)	Homogeneity (by Microscope)
1	14.5	75.0	10.5	homogeneous
2	46.4	36.4	17.2	?
3	63.4	22.3	14.3	homogeneous
4	45.9	41.0	13.1	homogeneous
5	21.6	65.0	13.4	homogeneous
6	52.2	37.1	10.7	homogeneous
7	5.6	83.9	10.5	homogeneous

(B) Heat Treatment:

The alloys were ferromagnetic as cast. The alloys, 1, and 7 were fairly magnetic, and the rest of the alloys, 2, 3, 4, 5, and 6, were only feebly magnetic as prepared. The alloys were homogenized at temperatures ranging from 900F to 1300F for three hours. Two specimens of each alloy were prepared; one quenched in water and the other cooled in the furnace after a three-hour homogenizing period. The magnetism of the alloys was determined qualitatively by a strong magnet, and each specimen was examined under the microscope.

All of the quenched specimens consisted of a single phase. As for the specimens cooled in the furnace, the alloys, 1, 3, and 7, were composed of a single phase and the rest of the alloys were composed of two phases.

With the exception of the alloys, 1, and 7, of both quenched and furnace-cooled specimens, the alloys were either nonmagnetic or feebly magnetic. One interesting fact in the microstructure of the alloys is that both quenched and furnace-cooled specimens of the alloys, 1, and 7, appeared to be the same. This fact implies the possible existence of the same phase from the quenching temperature to room temperature in both alloys. The quenched specimen of the alloy 5 was so brittle that preparation of a suitable specimen was difficult; however, it appeared to consist of a single phase under the microscope.

The results of the heat treatment are tabulated in Table IV. The phases listed in the table were identified either by the equilibrium diagrams or by X-ray results.

All of the quenched specimens were then aged at 400F for 52 hours, during which time,relative magnetization of the alloys, 1, 2, and 6, were measured by a magnetic balance. The results will be discussed in the next paragraph.

Table IV

Microstructure and Ferromagnetism
of the Heat-Treated Alloys

(1) Furnace-cooled Alloys:

Alloy No.	As Cast	Temp. F	Time hr.	Phase	Magnet.	Remarks
1	mag.	950	3	ε	mag.	fused 1100F
2	feebly mag.	1100	3	?	feebly mag.	
3	feebly mag.	1100	2	α	non mag.	
4	feebly mag.	1100	2	?	non mag.	
5	feebly mag.	1100	2	?	non mag.	fused 1300F brittle
6	feebly mag.	1100	2	?	feebly mag.	
7	mag.	900	3	ε	mag.	fused 950F

(2) Quenched Alloys:

1	mag.	950	3	ε	mag	fused 1100F
2	feebly mag.	1300	3	β	feebly mag.	
3	feebly mag.	1300	3	α	non mag.	
4	feebly mag.	1300	3	β	non mag.	
5	feebly mag.	1200	3	ε	feebly mag.	fused 1300F brittle
6	feebly mag.	1300	3	β	feebly mag.	
7	mag.	900	3	ε	mag.	fused 950F

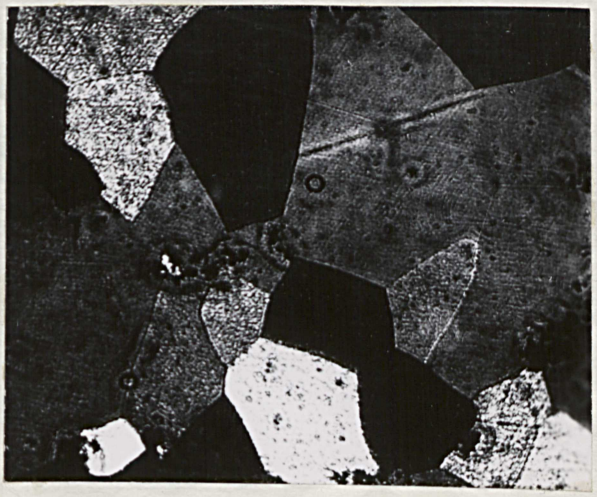


Fig. 3
Alloy 1, Cooled in Furnace from 950 F, 100 x
Ferric Chloride Etch

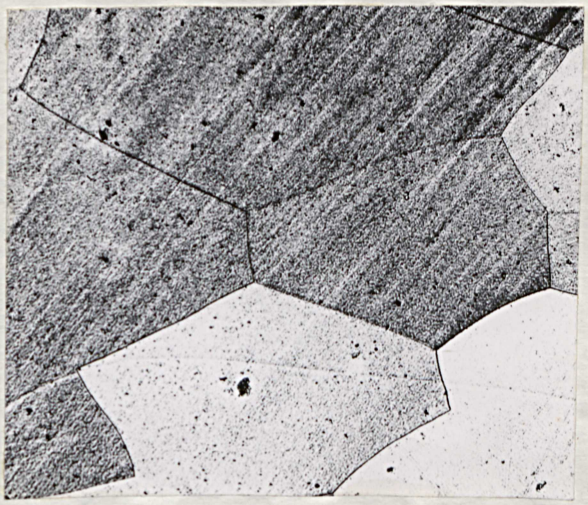


Fig. 4
Alloy 2, Quenched from 1300 F, 100 x
Potassium Dichromate Etch

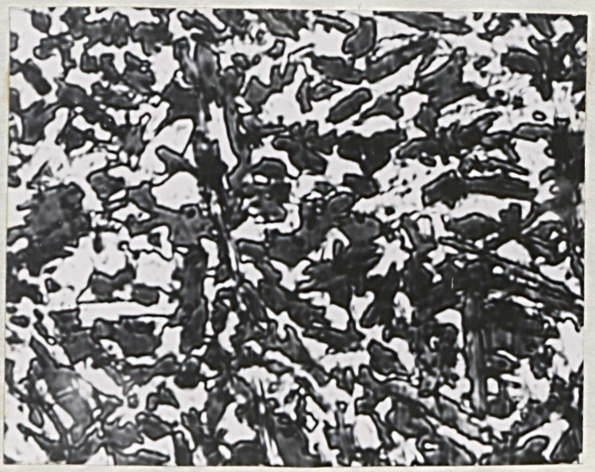


Fig. 5
Alloy 2, Cooled in Furnace from 1300 F, 500x
Ferric Chloride Etch

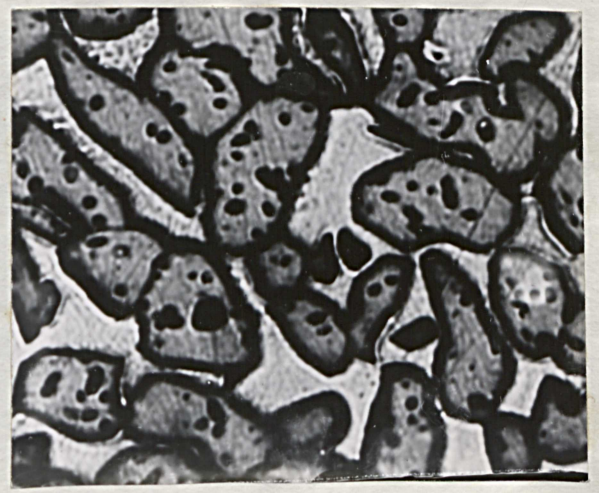


Fig. 6
Alloy 5, Cooled in Furnace from 1200 F, 500x
Ferric Chloride Etch

(C) Magnetic Work:

Relative change in magnetization was first qualitatively measured on the quenched specimens which were aged for varying periods of time at 400F. With the exception of the alloy 5, the change in ferromagnetism of the alloys was hardly detectable. However, a remarkable change in magnetic saturation was observed in the alloy 5 during aging.

Relative magnetic saturation values of the alloys, 1, 2, and 5, were determined by a magnetic balance constructed by Mr. E. Willner, senior in Metallurical Engineering, M.S.M.. It contains two coils wound on spools surrounding two pole pieces of Armco iron. One pole is made smaller than the other, and the end of the larger pole is made concave, so that an inhomogeneous field is produced upon magnetizing the pole pieces. When a small specimen is placed between the poles, it is attracted toward the small pole by the force given below:

$$F = m \cdot \sigma \cdot dH/dx \cdot H$$

Where, m: mass of specimen (g)

σ : magnetization (erg per gauss per gram)

dH/dx: rate of change of field intensity (orsted per cm)

H: field intensity (orsted)

If the value of dH/dx is made constant, the magnetization of a specimen of unit mass is directly proportional to the force. This force exerts a torsion in a thin wire which carries a mirror so that the torsional force is measured by deflection. The principle is similar to that of the d'Arsonval galvanometer. More detailed information may be obtained from Mr. Willner's thesis. The magnetic balance was not calibrated against standard values; hence, only relative values were obtained.

Before each measurement, magnetization of a small piece of nickel wire in terms of divisions per gram was determined. Relative magnetization of each alloy was calculated by dividing divisions of deflection per gram of alloys by that of nickel. The shape of specimen affects the results considerably; therefore, it is essential to use the same nickel piece in each measurement. The alloy 5 became very brittle and badly cracked during aging; therefore, for this specimen, a small nickel ball was used for standardization. The results are shown graphically in Fig. 7, Fig. 8, and Fig. 9.

The magnetization of the alloy 1 increased upto six-hours' aging, and approached a stable value. Whereas, the magnetization of the alloy 2 decreased rapidly and became nonmagnetic at the end of two-hours' aging.

FIG- 7

EFFECT OF AGING AT 400F ON MAGNETIZATION

ALLOY I

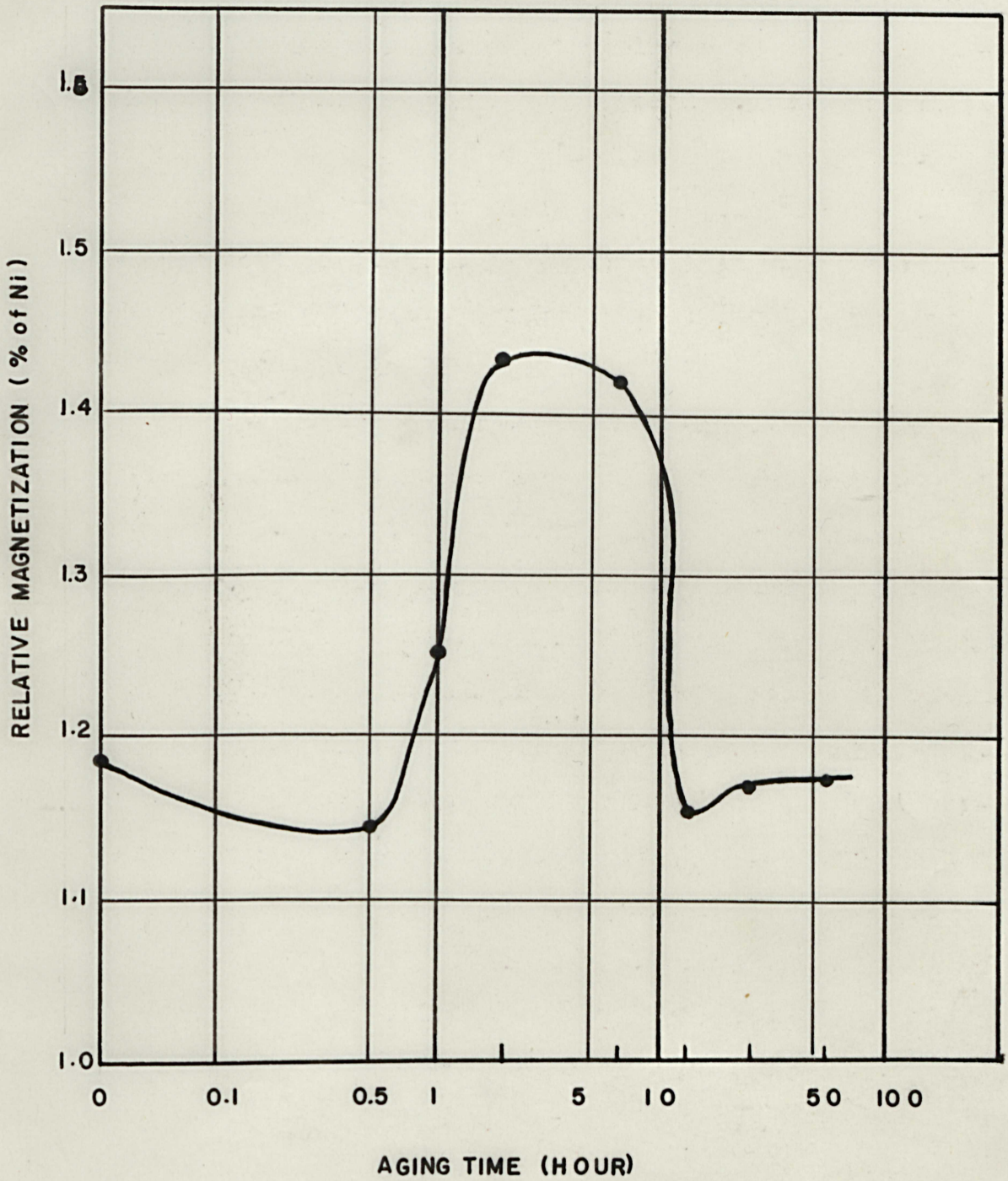


FIG-8

EFFECT OF AGING AT 400°F ON MAGNETIZATION

ALLOY2

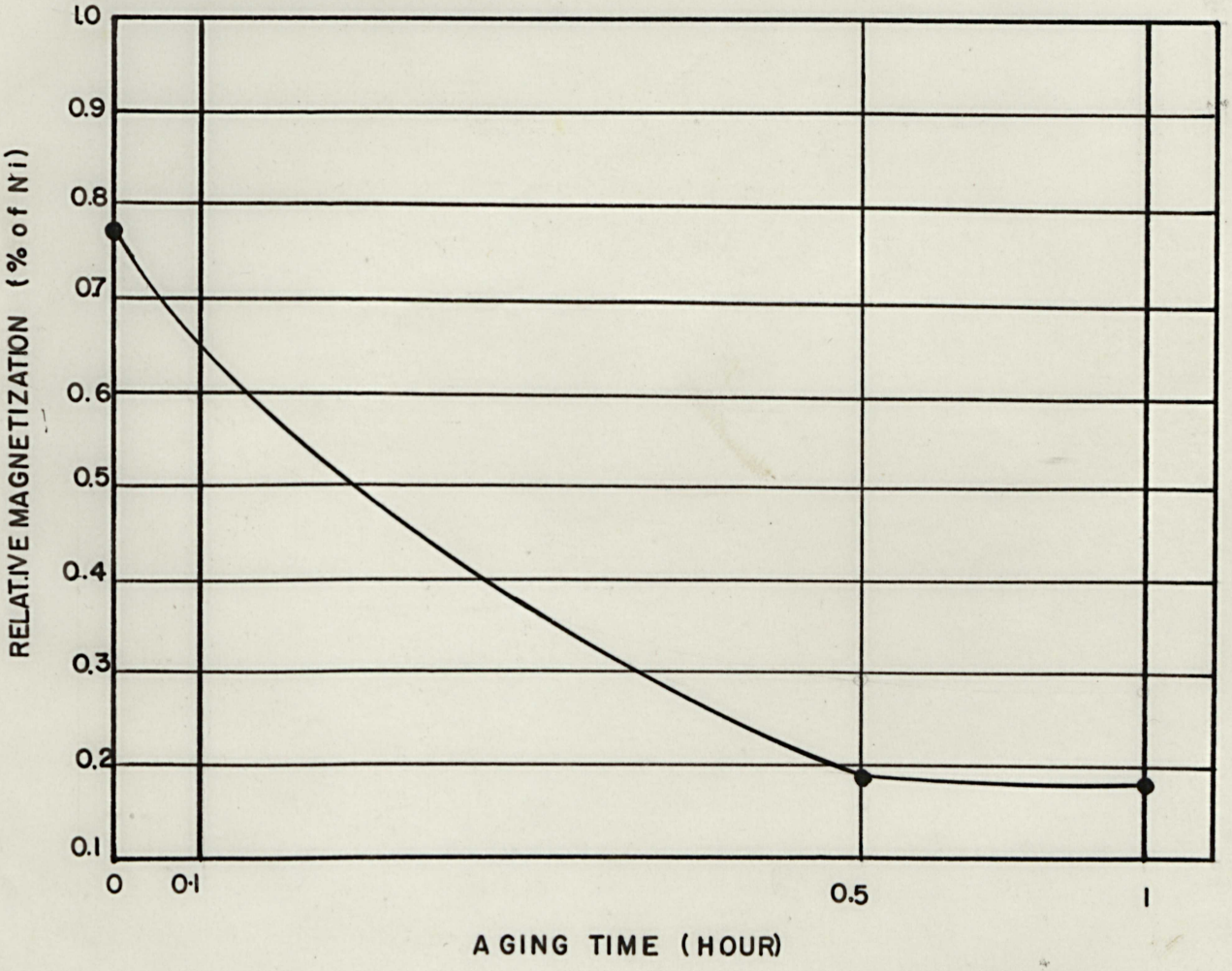
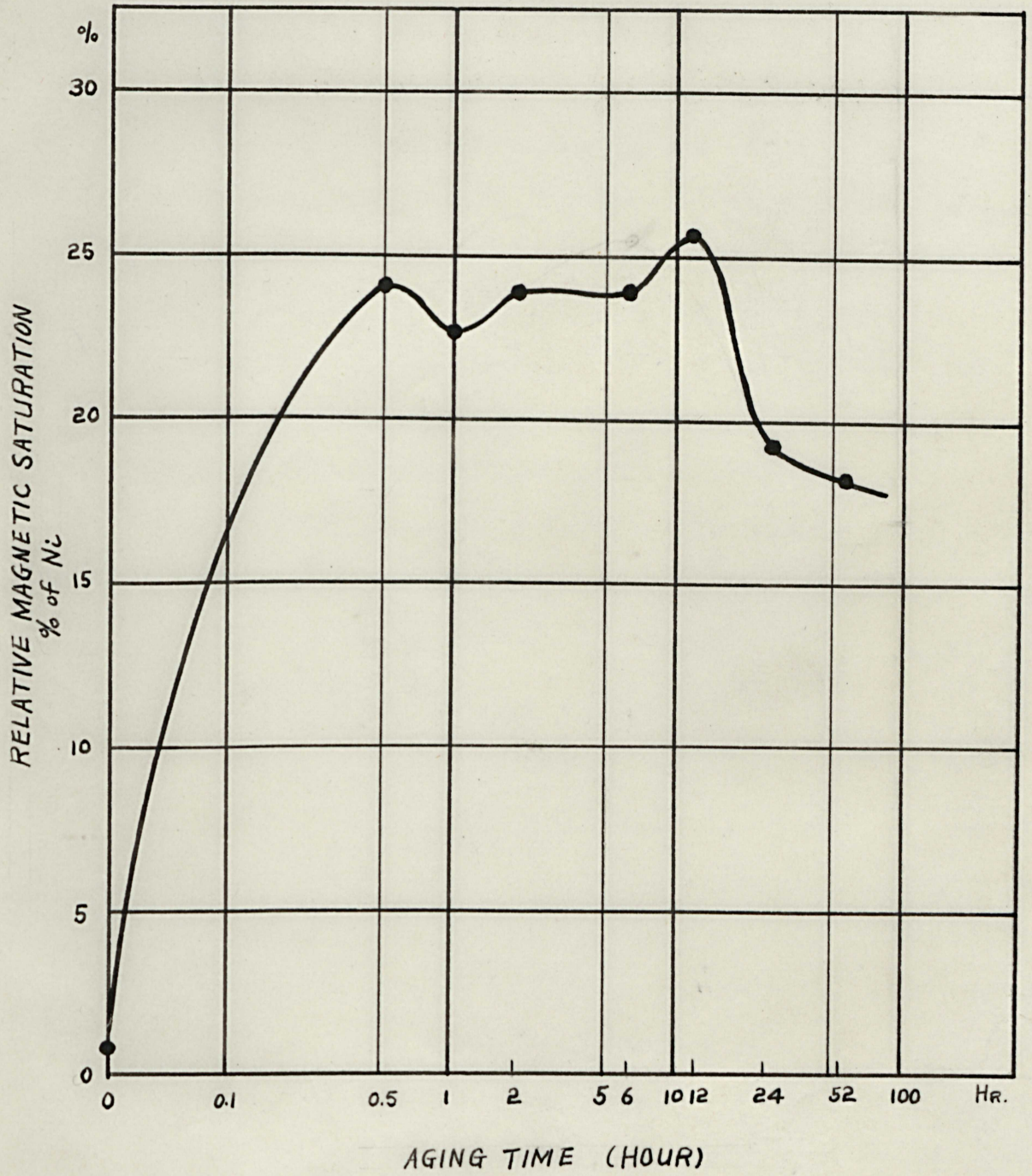


FIG-9

EFFECT OF AGING AT 400F ON MAGNETIZATION

ALLOY 5



However, the magnetitude of magnetization change was very small.

A notable increase in the magnetization was observed in the specimen of the alloy 5. Microscope examination showed no change in the microstructure of the alloy at the end of four-hours' aging; however, precipitation of a new phase was observed at the grain boundaries in the specimen aged for forty-two hours. An X-ray diffraction pattern of the alloy 5 aged for four hours and for eight hours showed many new lines besides the basic hexagonal-close-packed lines of the quenched specimen. This change will be discussed later.

(D) X-ray Work:

Powder-diffraction photographs of several magnetic specimens were taken by a cylindrical camera of 7 cm radius. Powders of -300 mesh were prepared by filing the alloys. Upon cold work, i.e., filing, the powder is likely to suffer a loss in magnetism, and shows other property changes; therefore, it should be annealed. But, no suitable glass containers that will withstand a high temperature were available at the time when the photographs were taken. Dr. Carapella reported that Pyrex

or Vitreosil tube were found to withstand temperatures as high as 750C for over a week without failure.(4)

However, the powder of the alloy 1 was sealed in vacuum, in an ordinary glass tube and given annealing at 400F for four hours.

Since this alloy consisted of a single phase at temperatures ranging from 950F to room temperature, it was assumed that there would be no phase change on annealing at 400F. Powder of the quenched alloy 5 was also annealed in vacuum at 400F for four hours and for eight hours.

The powder specimens were mounted on a glass fiber at the center of the camera with the aid of grease, and were rotated during exposure. All of the X-ray photographs were taken with a copper target, a current of 15 milliamperes, and a voltage of 40 kilovolts. Exposure time was two hours. Hull-Davey charts were used in identification of the powder patterns.(17) The charts are made with lattice-plane spacings plotted along the axis of abscissas according to a logarithmic scale, and different axial ratios --- $C = \frac{c}{a}$ --- appear at different vertical levels on the charts.

In the patterns of the unannealed powders, lines were widened and weakened; whereas, the annealed powder

patterns showed much sharper lines----this fact confirmed the effect of cold work.

X-ray photographs with diffraction data are shown in appendix.

IV. DISCUSSION OF RESULTS:

It was first intended to make alloys whose compositions are equal to Cu_2MnZn (51.5 wt.% Cu, 22.2 wt.% Mn, 26.4 wt.% Zn), and $Cu_2Mn_2Zn_5$ (approximately 22 wt.% Cu, 22 wt.% Mn, 56 wt.% Zn). However, as previously mentioned, none of the alloys above were obtained in their exact intended compositions. The closest alloys obtained for Cu_2MnZn were the alloys, 2 and 6, and for $Cu_2Mn_2Zn_5$, the alloy 5. The homogeneity of alloy 2 was, however, doubtful.

It was found that both the beta and epsilon phases were retained by quenching, and both phases are ferromagnetic on proper heat treatment.

(A) Epsilon Alloys:

Alloys of the epsilon phase are definitely ferromagnetic. The alloys, 1, 5, and 7, whose zinc contents are over 60%, are epsilon at elevated temperatures. The alloys, 1, and 7, are epsilon over a temperature range from 950F to room temperature. X-ray diffraction patterns show the crystal structure to be hexagon-close-packed with an axial ratio of approximately 1.60. Lattice constants a and c were calculated, and their values

are 2.744 Å and 4.358 Å respectively. Magnetic property of the alloys, 1, and 7, undergoes very little change on aging at 400F; however, the maximun saturation of the alloy 1 was attained at the end of two hours' aging at 400F. (Fig. 7)

X-ray pattern of annealed powder of the alloy 1, for four hours at 400F, shows quite different lines from those of the unannealed specimen. (Fig. 12, Table VII) Under the microscope, however, no apparent change in the structure was observed. The diffraction pattern could not be interpreted satisfactorily.

The alloy 5, whose composition is close to the alloy previously reported by O. Heusler as being most ferromagnetic, became strongly magnetic on aging. (Fig. 9) The maximun magnetic saturation of this alloy was 25% that of nickel at the end of twelve-hours' aging. The alloy was brittle as quenched with very feeble magnetism. Under the microscope, it appeared to consist of a single phase. X-ray powder photograph showed that the crystal structure was probably hexagonal-close-packed; however, because of severe cold work on the filing, the lines were blurred. (Fig. 15, Table X)

The powder pattern of the alloy 5, annealed for four hours reveals many different lines from those of

the basic hexagonal-close-packed structure. (Fig. 16, Table XI) The X-ray pattern of this alloy aged for eight hours is essentially the same as that annealed for four hours. (Fig. 17) However, under the microscope, no structure change was observed between the specimen as quenched and that aged for four hours. Upon forty-two hours' aging, a new phase appeared at the grain boundaries, and at which time, the magnetization value of the alloy was being lowered. The aged alloy 5 was very brittle. The X-ray powder pattern of the aged alloy could not be interpreted, but the basic hexagonal-close-packed lines were easily identified. (Table XI) The appearance of new lines can be suspected to indicate either a superstructure transformation or a phase change which could not be detected by microscopic examination; however, the data on hand is not sufficient for a complete explanation.

(B) Beta Alloys:

Beta alloys were ferromagnetic to a much smaller degree than the epsilon alloys; their degree being 0.5% of nickel. Specimens cooled in the furnace consisted of two phases. (Fig. 5) No attempt was made to identify

the products of beta phase decomposition at lower temperature. (Fig. 20, Table XIV)

X-ray results of the beta alloys were not very successful, because none of the patterns could be interpreted satisfactorily. In view of the analogy between Cu_2MnAl, Cu_2MnSn, Cu_2MnIn, and Cu_2MnZn, an attempt was made to find superlattice lines in the pattern of alloy 6 quenched from 1300F. (Fig. 21, Table XV) Lattice constant a was calculated (a = 6.12 Å), and the intensity F^2pU was calculated. But it was difficult to identify any lines. Moreover, it probably is difficult to interpret superlattice line, since the atomic scattering factors for each elements are too close together (f_{Cu} = 29, f_{Mn} = 25, and f_{Zn} = 30, when $\frac{\sin\theta}{\lambda} = 0$), unless a suitable X-ray target other than copper is used.

Upon aging at 400F, the beta alloys lose their magnetism rapidly as shown in Fig. 8. It is believed that decomposition of the beta phase resulted in a decrease of magnetization. A new phase was apparently precipitated out at the grain boundaries in the specimen of alloy 2 after forty-two hours' aging.

Hume-Rothery's law does not seem to apply to the alloys of the Cu-Mn-Zn system. If we assign normal

valencies to copper (1), manganese (0), and zinc (2), the electron concentration of the alloy 1 (approximately $CuMnZn_6$) will be 1.62 in contrast with the values according to the Hume-Rothery's law; namely, 1.5 for beta alloys and 1.75 for epsilon alloys. This contradiction was also reported by Carapella in the Cu-Mn-Sn alloys. (4)

Lattice constant a of the ordered Cu_2MnAl, Cu_2MnSn, and Cu_2MnIn reported previously was approximately 6.2 Å. (4,5,6) The calculated lattice constant a of the alloys, 2, and 6, --- 6.12 Å --- is fairly close to that value above. However, because of the lack of additional information as mentioned before, the comparison can not be made.

V. CONCLUSION:

With data obtained in this investigation, comparisons in ferromagnetism between the alloy of $Cu_2Mn_2Zn_5$ (approximate atomic percentage) and the alloy of Cu_2MnZn (exact atomic percentage) can not be made.

However, both beta phase and epsilon phase in the Cu-Mn-Zn system were found to be ferromagnetic, though, to a very smaller degree than the other Heusler alloys. Furthermore, the epsilon phase was more magnetic than the beta phase----their degree of ferromagnetism being about 1% of Ni for the epsilon, and 0.5% of Ni for the beta. The maximum ferromagnetic saturation was obtained in the alloy 5 which was quenched from 1200F and aged for twelve hours at 400F. The relative magnetic saturation value for this specimen was about 25% that of nickel.

The appearance of new lines in the X-ray diffraction pattern of this specimen (Fig. 16, 17, Table XI) requires further experiment and explanation. The author wishes to continue further research on the Cu-Mn-Zn alloys in future if possible.

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APPENDIX

X-RAY DIFFRACTION PHOTOGRAPHS

I. Epsilon Group:

Fig. 10: Alloy 1, Quenched from 950F

Fig. 11: Alloy 1, Cooled in Furnace

Fig. 12: Alloy 1, Aged at 400F for 4 Hours

Fig. 13: Alloy 7, Quenched from 850F

Fig. 14: Alloy 7, Cooled in Furnace

Fig. 15: Alloy 5, Quenched from 1200F

Fig. 16: Alloy 5, Aged at 400F for 4 Hours

Fig. 17: Alloy 5, Aged at 400F for 8 Hours

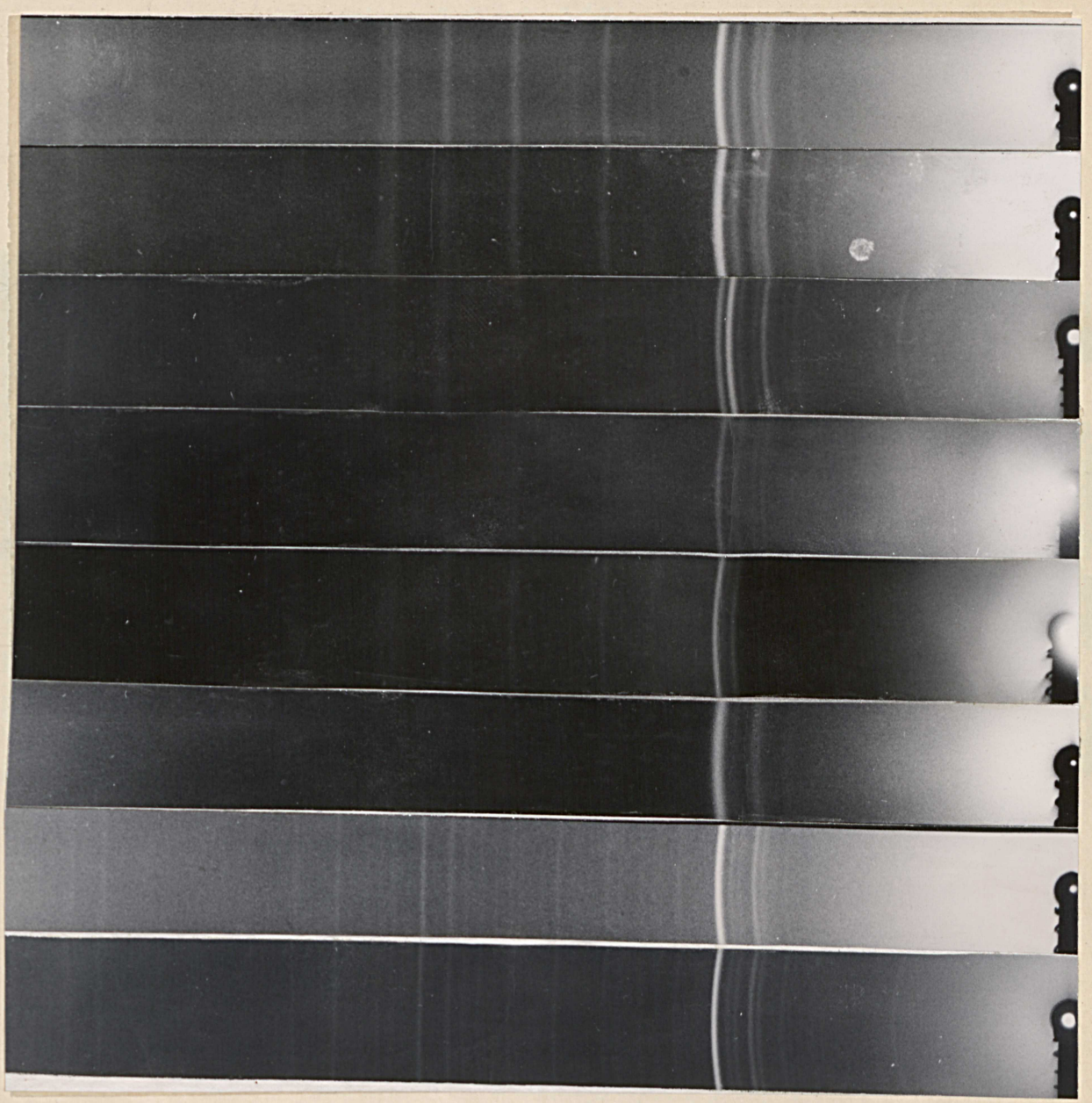
II. Beta Group:

Fig. 18: Alloy 2, Quenched from 1300F

Fig. 19: Alloy 2, Aged at 400F for 42 Hours

Fig. 20: Alloy 2, Cooled in Furnace

Fig. 21: Alloy 6, Quenched from 1300F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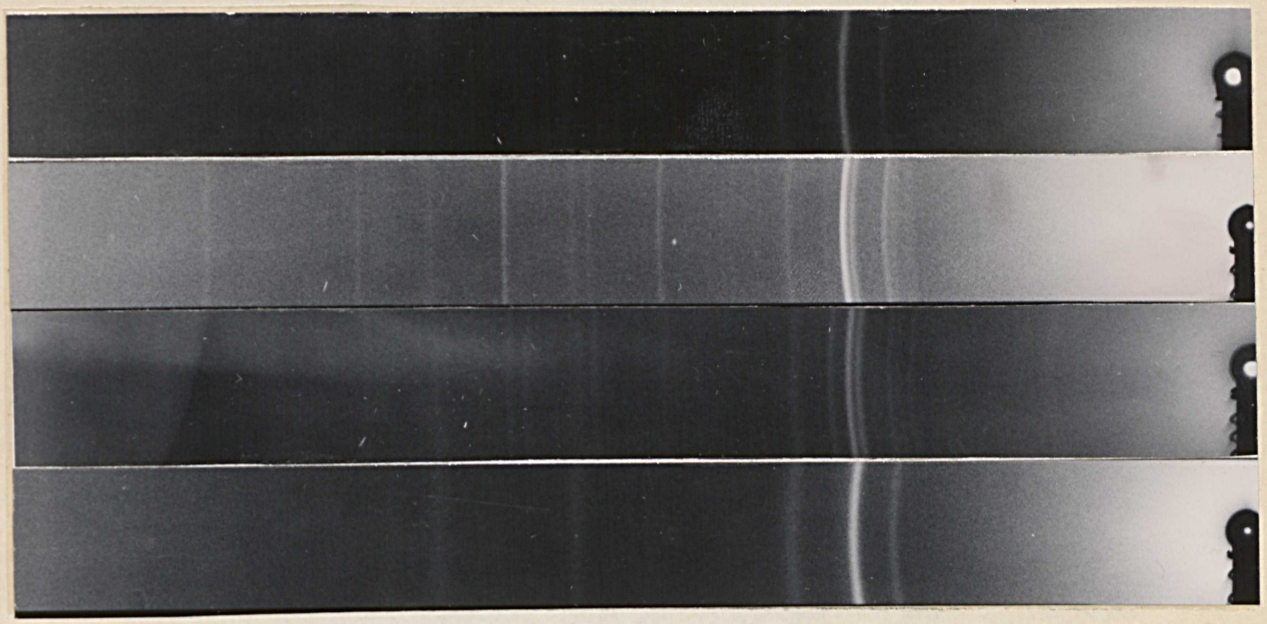
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Table V (Fig. 10)

X-ray Diffraction Data for Alloy 1, Quenched from 950F

Radiation	hkil	$d_{obs.}$	$d_{cal.}$	Intensity Obs.	Intensity F^2pU
Cu K β_1	$10\bar{1}0$	2.390	2.375	w	
α_1		2.390		s	220,500
β_1	$10\bar{1}1$	2.095	2.085	s	
α_1		2.097		ss	430,000
α_1	0002	2.170	2.176	s	55,000
β_1	$11\bar{2}0$	1.370	1.370	ww	
α_1		1.372		m	30,600
β_1	$11\bar{2}2$	1.163	1.160	ww	
α_1		1.162		m	32,600
α_1	$10\bar{1}3$	1.242	1.276	m	63,700
α_1	$20\bar{2}1$	1.15	1.16	m	47,250
α_1	0004	1.094	1.090	ww	4,420
α_1	$20\bar{2}2$	1.041	1.042	w	11,020
α_1	$10\bar{1}4$	0.988	0.980	ww	10,250
α_1	$20\bar{2}3$	0.922	0.920	w	28,750
α_1	$12\bar{3}1$	0.880	0.879	mw	30,500
α_1	$11\bar{2}4$	0.855	0.853	w	21,600

(continued)

H.C.P.

$(c/a)_{obs} = 1.59$

$a_{cal} = 2.744$ Å

$c_{cal} = 4.358$ Å

$(c/a)_{cal} = 1.598$ Å

Intensity was calculated as being proportional to F^2pU, where F is the structure factor, p is the number of cooperating planes, and U is the Lorentz-Polarization factor. The structure factor is calculated from the atomic percentage of the alloy which is close to $CuMnZn_6$, assuming the alloy is disordered. The equations used in calculating intensity will be given later.

Table VI (Fig. 11)

X-ray Diffraction Data for Alloy 1
Cooled in Furnace from 950F

hkil	Observed Intensity	Radiation	$d_{obs.}$
	w	Cu K α_1	2.825
$10\bar{1}0$	w	β_1	2.380
	s	α_1	2.380
$10\bar{1}1$	s	β_1	2.085
	ss	α_1	2.085
0002	s	α_1	2.180
$10\bar{1}2$	www	β_1	1.660
	m	α_1	1.606
$11\bar{2}0$	ww	β_1	1.374
	m	α_1	1.372
$10\bar{1}3$	w	α_1	1.240
$20\bar{2}0$	www	α_1	1.192
$11\bar{2}2$	w	α_1	1.164
$20\bar{2}1$	w	α_1	1.150
$20\bar{2}2$	www	α_1	1.039
$10\bar{1}4$	www	α_1	0.978
$20\bar{2}3$	www	α_1	0.920
$12\bar{3}1$	ww	α_1	0.880

H.C.P. ---- c/a = 1.59

Table VII (Fig. 12)

X-ray Diffraction Data for Alloy 1, Quenched from 950F, Aged for 4 hr. at 400F

Observed Intensity	$d_{obs.}$ (All for Cu K_{α_1})
WWW	4.775
m	4.17
WW	3.74
m	2.63
W	2.525
WWW	2.44
S	2.38
W	2.31
W	2.205
SS	2.145
S	2.08
W	1.986
W	1.945
WWW	1.900
W	1.860
WWW	1.770
WW	1.663
m	1.598
m	1.525
WWW	1.470
WWW	1.420
m	1.376
WWW	1.325
W	1.284
WW	1.275
m	1.244
m	1.23
W	1.157
W	1.145
W	1.123
WWW	1.094
WWW	1.075
WWW	1.061
W	0.915
W	0.878
WWW	0.862
WWW	0.855
W	0.848

Table VIII (Fig. 13)

X-ray Diffraction Data for Alloy 7, Quenched from 850F

hkil	Intensity	Radiation	$d_{obs.}$
$10\bar{1}0$	m	Cu $K\alpha_1$	2.400
$10\bar{1}1$	m	β_1	2.140
	ss	α_1	2.100
0002	s	α_1	2.217
	m	α_1	1.690
$11\bar{2}0$	m	α_1	1.378
$10\bar{1}3$	m	α_1	1.252
$20\bar{2}1$	m	α_1	1.158
0004	ww	α_1	1.103

H.C.P.

c/a = 1.60

Film was pre-exposed

Table IX (Fig. 14)

X-ray Diffraction Data for Alloy 7, Cooled in Furnace from 850F

hkil	Intensity	Radiation	dobs.	Remarks
$10\bar{1}0$	w	β_1	2.398	
	s	Cu K α_1	2.391	
$10\bar{1}1$	s	β_1	2.103	
	ss	α_1	2.100	
0002	s	α_1	2.202	
$10\bar{1}2$	w	β_1	1.620	
	w	α_1	1.620	
	www	α_1	1.573	existance of line very doubtful
$11\bar{2}0$	ww	β_1	1.385	
	m	α_1	1.380	
$10\bar{1}3$	m	α_1	1.252	
$11\bar{2}2$	m	α_1	1.173	
$20\bar{2}1$	m	α_1	1.153	

H.C.P.

c/a = 1.60

Table X (Fig. 15)

X-ray Diffraction Data for Alloy 5,
Quenched from 1200F

hkil	Intensity	Radiation	$d_{obs.}$	Remarks
	w	Cu $K\alpha_1$	2.660	
$10\bar{1}1$	s	β_1	2.097	
	ss	α_1	2.092	
0002	w	α_1	2.185	
	www	α_1	1.900	existence of line very doubtful
	www	α_1	1.747	existence of line very doubtful
$10\bar{1}2$	w	α_1	1.595	
	ww	α_1	1.482	
$11\bar{2}0$	ww	α_1	1.360	
	www	α_1	1.282	existence of line very doubtful
$10\bar{1}3$	www	α_1	1.240	
	w	α_1	1.205	probably 0003
$20\bar{2}1$	ww	α_1	1.136	
0004	ww	α_1	1.092	

Probably H.C.P.

c/a = 1.60

Effect of severe cold work was very Pronounced

Table XI (Fig. 16)

X-ray Diffraction for Alloy 5, Quenched from 1200F, Aged for 4 hr. at 400F

hkil	Intensity	$d_{obs.}$ (All for Cu K_{α_1})
	www	2.795
	w	2.554
	w	2.470
$10\bar{1}0$	m	2.371
$10\bar{1}1$	s	β_1 2.088
	ss	α_1 2.085
	m	2.228
0002	m	2.195
	www	1.975
	m	1.880
	w	1.811
	w	1.740
	w	1.660
$10\bar{1}2$	w	1.615
	m	1.480
	w	1.435
	ww	1.395
$11\bar{2}0$	w	1.368
	w	1.340
	w	1.310

(continued)

hkil	Intensity	d_{obs} (All for Cu K_{α_1})
	w	1.280
$10\bar{1}3$	m	1.250
	s	1.210
$20\bar{2}0$	w	1.191
$11\bar{2}2$	w	1.166
$20\bar{2}1$	w	1.145
	ww	1.130
	www	1.113
0004	m	1.092
	www	1.077
$20\bar{2}2$	w	1.045
	www	1.019
$10\bar{1}4$	www	1.001
	www	0.970
$20\bar{2}3$	www	0.926
$12\bar{3}0$	m	0.897
$12\bar{3}1$	m	0.880
	www	0.864
$11\bar{2}4$	www	0.854
$12\bar{3}2$	m	0.832
$30\bar{3}0$	m	0.791

(hkil) is for a hexagonal-close-packed structure of an axial ratio 1.60

Table XII (Fig. 18)

X-ray Diffraction Data for Alloy 2, Quenched from 1300F

hkl	Intensity	Radiation		$d_{obs.}$
110	m	CuK	β_1	2.165
	ss		α_1	2.165
	m			1.882
	www			1.714
	m			1.324
	m			1.132
220	w		α_1	1.085

(hkl) is for a disordered body-centered-cubic structure

Table XIII (Fig. 19)

X-ray Diffraction Data for Alloy 2, Quenched from 1300F, Aged for 42 hrs. at 400F

Intensity	$d_{obs.}$ (All for Cu K_{α_1})
ww	2.455
w	2.368
s	2.310
s	2.13
ss	2.085
ww	2.005
www	1.906
m	1.850
ww	1.746
ww	1.667
ww	1.632
s	1.475
m	1.339
m	1.305
ww	1.266
www	1.230
s	1.206
m	1.114
ww	1.064
m	1.046
m	0.935

Table XIV (Fig. 20)

X-ray Diffraction Data for Alloy 2, Cooled in Furnace from 1300F

Intensity	$d_{obs.}$ (All for Cu $K\alpha_1$)
ww	4.080
w	2.47
ww	2.385
w	2.32
www	2.210
s	2.15
ss	2.095
m	2.01
m	1.86
w	1.48
www	1.418
w	1.337
w	1.312
w	1.23
w	1.206
ww	1.118
www	1.072
ww	1.042

Table XV (Fig. 21)

X-ray Diffraction Data for Alloy 6, Quenched from 1300F

Intensity	$d_{obs.}$ (All for Cu K_{α_1})
m	2.390
ss	2.16
m	1.880
www	1.780
www	1.580
ww	1.463
www	1.390
m	1.322
www	1.257
www	1.182
m	1.130
m	1.081
www	1.032

II. Data for the Magnetic Saturation Measurement:
(Aging at 400F, Current: 0.1475 milliamp.)

Alloy 1				TIME				
	As Q.	30min	1hr	2hr	6hr	12hr	24hr	52hr
Wt.(g)	3.2215							
Ave.Div.	264.7	183.1	199.0	196.5	198.8	195.2	198.3	182.2
Div./g	82.1	56.8	61.9	61.0	61.7	60.6	61.6	56.6
#1/Ni_1	.0118	.0114	.0125	.0143	.0142	.0115	.0117	.0117
Alloy 2								
Wt.(g)	1.9055							
Ave.Div.	97.3	18.5	18.3					
Div./g	51.0	9.71	9.60					
#2/Ni_1	.0077	.00198	.00193					
Ni $wire_1$								
Wt.(g)	.0715	.0378						
Ave.Div.	500.6	185.4	187.4	161.7	164.0	198.3	199.9	181.6
Div./g	7000	4910	4960	4280	4340	5250	5280	4810
Alloy 5								
Wt.(g)	1.6008	.2995	.2980	.2555	.2555	.2555	.2500	.2220
Ave.Div.	97.3	276.6	276.8	241.4	253.8	293.2	280.5	166.7
Div./g	60.80	924	929	945	992	1146	1001	751
#5/Ni_2	0087 (#5/Ni_1)	.242	.227	.238	.234	.255	.193	.183
Wt.(g)	Ni $wire_2$ .0715	Ni $ball_2$ .0995						
Ave.Div.	500.6	378.8	405.0	393	421.3	447.7	515.7	408.1
Div./g	7000	3810	4080	3950	4230	4500	5180	4110

III. Formulas for Calculation of the Intensity of X-Ray Pattern

A) Structure Factor (F) :

An impinging beam of X-rays accelerates the electron in an atom with a vibratory motion, and the electron vibration causes scattering of energy from the impinging beam. In a unit cell, each atom scatters with an amplitude proportional to f, or atomic scattering factor, which approaches the atomic number Z when the angle of incident of a beam becomes zero. The intensity of X-ray is proportional to the square of the resultant vector of all the diffracted rays from individual atoms in a unit cell; this resultant vector is called the structure factor (F), and is expressed mathematically as follows:

$$|F|_i^2 = \left[\sum f_i \cos 2\pi(hu_i + kv_i + lw_i)\right]^2 + \left[\sum f_i \sin 2\pi(hu_i + kv_i + lw_i)\right]^2$$

Where, h, k, and l are the Miller indices, and u, v, and w are the coordinates of the atoms.
For a hexagonal-close-packed system, (u,v,w) is (0,0,0) and (2/3, 1/3, 1/2). Then the structure factor becomes as follows:

$$|F|_i^2 = \left[f_i \cos 2\pi(0) + f_i \cos 2\pi(2h/3 + k/3 + l/2)\right]^2 + \left[f_i \sin 2\pi(0) + f_i \cos 2\pi(2h/3 + k/3 + l/2)\right]^2$$

(B) Cooperating Planes (p):

The intensity of X-ray is also proportional to a number of planes which will diffract the ray to a same spot on a photographic film. In the powder method, all planes of same interplanar spacing will contribute the same ring on the film. These planes are called cooperating planes (p). Any higher order reflections from any given plane will have the same number of p. For a hexagonal-close-packed structure, p will be as follows:

h k l	p
h k l	24
00l	2
11O, $\bar{1}$1O	6
kkO, hhl, h$\bar{h}$l	12

(C) The Lorentz Polarization Factor (U):

If the radius of a cylindrical powder camera is R, the film will intersect a circle of circumference $2\pi R\sin 2\theta$. The energy per centimeter along the circumference of this circle will be inversely proportional to the sine of the glancing angle (θ), and to

the length of the circumference ($2\pi R\sin 2\theta$), in other words, the blackening of the powder diffraction line will be proportional to the product of two factors or so-called Lorentz Factor (U).

$$U = 1 + \cos^2 2\theta / \sin^2\theta \cos\theta$$

(D) Intensity (I):

As seen above, the intensity of the lines on an X-ray film in powder method is proportional to the structure factor (F), numbers of cooperating planes (p), and the Lorentz factor (U).

$$I \propto F^2 \cdot p \cdot U$$

For H.C.P. structure,

$$d_{hkl} = 1/\left[4/3a^2(h^2 + hk + k^2) + l^2/c^2\right]^{1/2}$$

VI. Etchants:

ASTM (1949)

Cu etchant No.1

NH_4OH.....5 parts
H_2O_2 .....2 -5
H_2O 5

No. 11

$FeCl_3$.....5 g
Ethyl alcohol.96 ml
HCl .....2 ml

Zn etchant No. 4

HNO_3 .....1 drop
Alcohol .....10 ml